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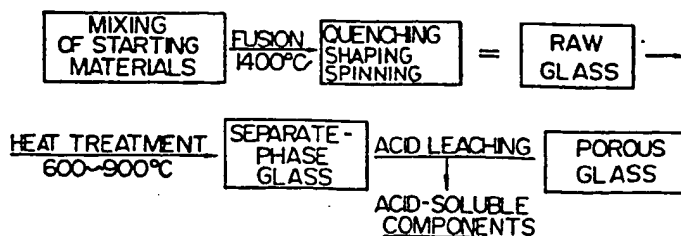
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54 Porous titanate glass and a method of producing it.

57 A porous titanate glass has a glass skeleton composed mainly of titania (TiO_2) and silica (SiO_2), in which the glass composition ratio (weight %) $\text{TiO}_2/\text{SiO}_2$ is 0.8 to 1.7, and said glass can be made in sheet or fiber form. To make the glass, a mixture of starting materials including TiO_2 and SiO_2 , e.g. together with Al_2O_3 , B_2O_3 , B_2O_3 and CaO is prepared, heated and fused and then quenched to form a raw multi-

component oxide glass composed of said vitrified oxides. The oxide glass is then heat-treated for a period sufficient to form an opaline or devitrified separate-phase glass which is thereafter acid-treated to leach out acid-soluble components, leaving the required porous glass product.

FIG. 1



"POROUS TITANATE GLASS AND A METHOD OF PRODUCING IT"

The present invention relates to porous titanate glass and a method of producing it. The titania-containing porous glass (referred to as porous titanate glass hereinafter) has a glass skeleton composed mainly of titania and silica, and the invention extends to sheets and fibers of such glass, and method of producing them.

A porous glass having an indefinite number of pores with a pore size of several Angstroms to several thousands of Angstroms ($1 \text{ \AA} = 0.1 \text{ nm}$) has already been proposed as suitable for use (inter alia) as adsorbents, catalysts, catalyst supports, gas sensors, ultrafiltration media, and carriers for immobilized enzymes. Such porous glasses are generally made from oxide glass. Those made of a $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O}_3$ composition system and those produced from a $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{CaO} - \text{MgO}$ composition system are known and in practical use. All of these porous glasses have a high silica content and are used for the production of high silica glasses such as Vaycor glass or the like. Such porous glasses that are produced from the $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O}$ composition system and the $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{CaO} - \text{MgO}$ composition system are characterized by their pore size

and specific surface area being controllable by regulating the heat treatment conditions during the phase separation process during which time they have relatively large pores.

- 5 However, when producing a porous glass from the $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O}$ and $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{CaO} - \text{MgO}$ composition systems, the raw fused glass has the disadvantage of exhibiting such a high viscosity it is difficult to remove bubbles,
10 resulting in requiring a fusion process of more than two hours at $1,500^\circ\text{C}$.

- Instead of producing a porous glass having a glass skeleton containing a high proportion of silica by the above described manufacturing method, it has
15 also been proposed to provide a porous glass having a glass skeleton produced from a titania gel or metal alcoxide. However, such porous glasses had the disadvantage of requiring a prolonged time for vitrification, and controlling the pore size of
20 the glasses was difficult.

- After extensive research and experiments in an attempt to overcome the foregoing shortcomings of the conventional porous glasses and methods of producing them, the inventor has developed a titania-containing
25 porous glass having titania and silica as a glass

skeleton in which the glass composition ratio of titania to silica may be in the range of 0.8 to 1.7, in distinct contrast to the high silica content porous glass produced by utilizing the phase separation of the conventional oxide glass, or the porous glass having a titania glass skeleton produced from titania or metal alcoxide.

The porous titanate glass (titanic acid - containing porous glass) of this invention provides a higher heat resistance and chemical resistance as well as a higher chemical reactivity because of its Ti-OH group as compared with the prior art porous glasses.

Through further research and experiments conducted on methods of producing porous titanate glass having the advantages as described above, it has been found that such porous glass may be very efficiently produced from a five-component composition of TiO_2 - SiO_2 - Al_2O_3 - B_2O_3 - CaO or a six-component composition of TiO_2 - SiO_2 - Al_2O_3 - B_2O_3 - CaO - MgO (or alkali metal oxide or metallic element oxide).

The present inventor has also conducted research and experiments with a view to overcoming the problems involved in making the porous titanate glass into sheet and fibers. The problems include difficulties with the fusing step, a tendency for crystallization to

occur during the quench-vitrification step, and a tendency for cracking and delaminating to take place during the acid treating step. It has been found that cracking and delaminating are attributed primarily
5 to the crystallization and the expansion of glass during the acid treating step and that such cracking and delaminating may be prevented by prescribing for the composition of the raw material for glass according to this invention.

10 This invention has aimed to provide a porous titanate glass which provides high heat resistance and chemical resistance (alkali resistance) as well as high chemical reactivity, and to provide a method of producing the titanate glass in an efficient
15 manner while controlling the pore size and specific surface area thereof.

Desirably, a method according to the invention can produce such porous titanate glass of homogeneous quality in a shortened time.

20 Beneficially, a method according to the invention can produce a porous titanate glass in which the raw materials are easily fusible, and which is less liable to crystallize during the fusing step and has very little tendency to crack during the acid treating step.

25 The invention also aims to provide sheets and

- fibers of porous titanate glass having titania and silica as a glass skeleton, and which have a wide range of applications as catalysts, gas sensors, reaction separating membranes, adsorbents and the like.

According to the present invention, there is provided porous titanate glass characterized by having a glass skeleton composed mainly of titania (TiO_2) and silica (SiO_2). The invention comprehends sheets and fibers having such a glass skeleton.

Such porous titanate glass can be produced from a six-component composition of TiO_2 - SiO_2 - Al_2O_3 - B_2O_3 - CaO - MgO .

The glass composition ratio (weight %) $\text{TiO}_2/\text{SiO}_2$ may be in the range of 0.8 to 1.7.

The following description is given by way of example of preferred features of the invention.

This porous titanate glass may be produced efficiently by mixing starting materials containing titanium oxide (TiO_2), silicic anhydride (SiO_2), aluminum oxide (Al_2O_3), boron oxide (B_2O_3), and calcium oxide (CaO); heating and fusing the materials, followed by quenching them to form a multi-component oxide glass composed of a five-component composition of vitrified TiO_2 - SiO_2 - Al_2O_3 - B_2O_3 - CaO ; reheating

the oxide glass at a temperature of 600°C to 900°C for a predetermined period of time to form an opaline or devitrified separate-phase glass; and then immersing the separate-phase glass in an acid solution to leach
5 out and remove acid-soluble components.

Preferably, the starting materials contain 25.0 mol % of titanium oxide, 31.0 mol % of silicic anhydride, 12.5 mol % of aluminum oxide, 7.5 mol % of boron oxide, and 24.0 mol % of calcium oxide.

10 Alternatively, the aforesaid porous glass may be produced by a method comprising the steps of mixing starting materials containing for their principal components titanium oxide, silicic anhydride, aluminum oxide, boron oxide and calcium oxide and for
15 their accessory components at least one of magnesium oxide, alkali metal oxide and metallic element oxide, heating and fusing the material, followed by quenching it to form a multi-component oxide glass having a composition of vitrified $\text{TiO}_2 - \text{SiO}_2 - \text{Al}_2\text{O}_3 -$
20 $\text{B}_2\text{O}_3 - \text{CaO} - \text{MgO} - \text{X}_2\text{O} - \text{Y}_m\text{O}_n$ (wherein X_2O is alkali metal oxide and Y_mO_n is metallic element oxide), reheating said oxide glass at a temperature of 600°C to 900°C for a predetermined period of time to form an opaline or devitrified separate-phase glass,
25 and then immersing said separate-phase glass in an

acid solution to leach out and remove acid-soluble components.

Preferably according to this particular method, the starting materials may contain 15-34 mol % of titanium oxide, 17-34 mol % of silicic anhydride, 5-20 mol % of aluminum oxide, 1-10 mol % of boron oxide, 10-30 mol % of calcium oxide, 10 or less mol % of magnesium oxide, 5 or less mol % of alkali metal oxide, and 5 or less mol % of metallic element oxide. Preferably, the ratio of silicic anhydride to titanium oxide ($\text{SiO}_2/\text{TiO}_2$) is 0.4 to 2.0.

More specifically, sheets of porous titanate glass as described above may be produced by mixing starting materials containing titanium oxide, silicic anhydride, aluminum oxide, boron oxide, calcium oxide and magnesium oxide so that the composition of the materials on the basis of mol % of the oxides is such that $(\text{TiO}_2 + \text{SiO}_2)/(\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3 + \text{CaO} + \text{MgO})$ is 1.20 to 1.40, $\text{TiO}_2/\text{SiO}_2$ is 0.5 to 1.0, $\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3$ is 1.0 to 0.6 and MgO/CaO is 0.21 to 0.06, heating and fusing the mixture, then quenching and shaping it to form a sheet of multi-component oxide glass composed of vitrified $\text{TiO}_2 - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{CaO} - \text{MgO}$, reheating said oxide glass in sheet form at a temperature of 600°C to 900°C , preferably 700°C to 850°C ,

more preferably 750°C to 800°C for a predetermined period of time to form an opaline or divitrified separate-phase glass, and then immersing said separate-phase glass in an acid solution to leach
5 out and remove acid-soluble components.

Fibers of porous titanate glass as described above may be produced by mixing starting materials containing titanium oxide, silicic anhydride, aluminum oxide, boron oxide, calcium oxide and magnesium oxide
10 so that the composition of the materials on the basis of mol % of the oxides is such that $(\text{TiO}_2 + \text{SiO}_2) / (\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3 + \text{CaO} + \text{MgO})$ is 1.20 to 1.40, $\text{TiO}_2/\text{SiO}_2$ is 0.5 to 1.0, $\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3$ is 1.0 to 0.6 and MgO/CaO is 0.21 to 0.06, heating and fusing the
15 mixture, then spinning and quenching it to form fibers of multi-component oxide glass composed of vitrified $\text{TiO}_2 - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{CaO} - \text{MgO}$, reheating said fibrous oxide glass at a temperature of 600°C to 900°C, preferably 700°C to 850°C, more preferably 750°C to 800°C
20 for a predetermined period of time to form opaline or divitrified separate-phase glass fibers, and then immersing said separate-phase glass in an acid solution to leach out and remove acid-soluble components.

In the aforesaid methods of producing sheet and
25 fibers of porous titanate glass, the ratios of

B_2O_3/Al_2O_3 and MgO/CaO are preferably decreased as the ratio of TiO_2/SiO_2 is increased from 0.5 to 1.0.

Optionally, a part (about 0.5 mol %) of SiO_2 may be substituted for by metallic element oxide
5 such as MoO_3 , SeO_3 , Ni_2O_3 or the like, e.g. 0.5 - 1 mol % thereof, so that the metallic element oxide is supported on the porous glass skeleton to reduce delaminating.

In the aforesaid methods of producing porous
10 titanate glass in sheet or fibrous form, the mix of starting materials may comprise 18.0 - 28.0 mol % of titanium oxide, 38.0 - 28.0 mol % of silicic anhydride, 10.0 - 12.5 mol % of aluminum oxide, 7.5 mol % of boron oxide, 21.0 - 22.5 mol % of calcium
15 oxide, and 4.5 - 1.5 mol % of magnesium oxide.

Suitable raw materials which may be used in this invention are as follows, although this invention is not limited to these materials:

The titanium oxide source may include oxides,
20 hydroxides, alkoxides, and carbonate of titanium, and the like.

The silicic anhydride source may include silica sol, fumed silica, silica gel, alkoxides of silicon, feldspar, volcanic ash and the like.

25 The aluminum oxide source may include aluminum

alkoxides, pseudo-boehmite, alumina gibbsite,
sodium aluminate, alumino-phosphates and the like.

A boron oxide source may include boron oxide;
boric acids such as ortho boric acid, meta boric
5 acid, tetra boric acid; borax; borates such as
lithium, sodium and potassium borates, metaborates
and tetraborates e.g. of sodium; and the like.

A phosphoric acid source may include calcium
phosphates such as calcium hydrogenphosphate,
10 magnesium phosphates, aluminum phosphates, alkali metal
phosphates and the like.

The calcium oxide source may include calcium
carbonate, calcium phosphates and the like.

The magnesium oxide source, alkali metal oxide
15 source and metallic element oxide, when they are used
in practising this invention, may include oxides,
alkoxides, carbonates, nitrates, carboxylates,
phosphates, aluminates and silicates of those metals
and the like. The term "alkali metal" herein used is
20 intended to include lithium, sodium, potassium and
the like. The term "metallic element" is intended
to include metals other than the metals specifically
mentioned above, that is, titanium, calcium, magnesium
and the like alkali metals. By way of example, they
25 are metals in Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB,

IIA, IIIA, IVA, VA, the iron family and platinum group of the periodic Table of the Elements.

Particularly suitable are copper, silver, gold, zinc, cadmium, yttrium, germanium, tin, lead, zirconium, 5 bismuth, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium, platinum, lanthanide, actinide and the like.

The pore size and specific surface area of 10 porous titanate glass may be controlled by regulating the heat treating conditions for the phase separating step during the manufacturing process. In addition, the fused glass material according to this invention has such a low viscosity that it is easy to remove bubbles 15 and produce a homogeneous glass in 30 to 60 minutes of fusion process at $1,400^{\circ}\text{C}$. Thus, the present invention is capable of producing a porous titanate glass in an energy-saving manner as compared with the production of conventional porous glass.

20 The invention will be explained in more detail in the following non-limitative description, which is given by way of example, taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a block diagram illustrating the 25 process of producing a porous titanate glass according

to this invention;

Fig. 2 is a graph showing changes in the specific surface area due to the adjustments of the heat treatment temperature (phase separation
5 temperature) for porous titanate glass according to this invention;

Fig. 3 is a graph showing changes in average pore radius due to adjustments of the heat treatment temperature (phase separation temperature) for porous
10 titanate glass according to this invention;

Fig. 4 is a graph showing the results of thermogravimetric (TG) analysis and differential thermal analysis (DTA) conducted on the porous titanate glass according to this invention and on commercially
15 available silica glass;

Fig. 5 is a graph showing the alkali resistances of the porous titanate glass according to this invention and of a commercially available silica glass;

20 Fig. 6 is a graph showing changes in the specific surface area due to adjustments of the heat treatment temperature (phase separation temperature) for another porous titanate glass according to this invention;

25 Fig. 7 is a graph showing changes in the average

pore radius due to adjustments of the heat treatment temperature (phase separation temperature) for another porous titanate glass according to this invention;

5 Fig. 8 is a graph showing the changes in the distribution of pore sizes due to adjustments of the heat treatment temperature (phase separation temperature) for porous titanate glass of this invention; and

10 Fig. 9 is a graph showing the alkali resistances of another porous titanate glass according to this invention and of a commercially available silica glass.

Example 1

 Fig. 1 illustrates successive steps of the present manufacturing process for porous titanate glass.

 Starting materials containing 25.0 TiO_2 - 31.0 SiO_2 - 12.5 Al_2O_3 - 7.5 B_2O_3 - 24.0 CaO (mol composition) were thoroughly mixed together in a ball mill or the like. The mixture was then fused by heating in an electric furnace at 1400°C for 30 to 60 minutes, and quenched by placing it in a water bath, followed by shaping it to form a transparent raw glass. Subsequently, when the raw glass was

25 heated at a

temperature of 600°C to 900°C for a predetermined period of time in the range of 0.5 to 100 hours, changing it from its transparent state to an opaline or devitrified state whereby a separate-phase glass was obtained. This separate-
5 phase glass was immersed in a hydrochloric acid solution at 90°C for 1 to 2 hours to leach out and remove acid-soluble components, whereby a porous glass having a glass skeleton of acid-insoluble TiO_2 and SiO_2 remaining therein was produced.

It was found that the thus produced porous titanate
10 glass had a composition (weight %) of 37.5 TiO_2 - 46.0 SiO_2 - 14.3 Al_2O_3 - 2.17 CaO .

The composition analysis of the foregoing starting materials and porous titanate glass was carried out by X-ray fluorescence analysis .

15 As stated hereinabove, the porous titanate glass according to this invention makes it possible to control the pore size and specific surface area by regulating the heat treatment conditions (heating temperature and time) for the phase separation step, as shown in Figs. 2 and 3.

20 Fig. 2 shows the changes in the specific surface area of porous titanate glass as the heat treatment conditions for the phase separation are varied when producing a porous titanate glass using the raw material composition as described above. Fig. 3 shows the changes in the average pore radius
25 of porous titanate glass as the heat treatment conditions for

the phase separation are varied when producing a porous titanate glass using the same material composition as for Fig. 2. The heat treating time was twelve hours for either case. The average pore radius was measured using a soaped
5 mat.

As is seen from Figs. 2 and 3, as the heat treatment temperature rises, the specific surface area decreases whereas the pore radius increases. It is thus possible to produce a porous titanate glass having any desired pore
10 structure with a specific surface area ranging from $500 \text{ m}^2/\text{g}$ to $10 \text{ m}^2/\text{g}$ and a pore radius ranging from 20 \AA to 500 \AA (2 to 50 nm) by changing the heat treatment temperature and heating time.

The heat resistance and chemical resistance characteristics of the porous titanate glass produced by the method
15 of this invention will be discussed below.

Fig. 4 shows the changes in weight (heat resistance characteristics) versus changes in temperature for porous titanate glass produced according to the present invention. The curve (a) in the graph represents the porous titanate
20 glass while the curve (b) represents a commercially available high silica glass.

The curves indicate the results of thermogravimetric (TG) analysis and differential thermal analysis (DTA) in which samples each weighing 80 mg were used. The samples were
25 heated to 400°C in a DTA furnace and then cooled down, followed

by measuring the samples at a heating-up rate of 5°C/min and with DTA sensitivity of ± 25 μ V.

The commercially available high silica glass, which had been subjected to a heat treatment at a temperature of about 5 600°C exhibited no noticeable change in weight at temperatures between 500°C and 600°C, but showed a higher rate of weight change at temperatures exceeding 700°C. On the other hand, the porous titanate glass exhibited less changes in weight at temperatures between 650°C and 855°C, which showed that 10 it maintained a more stable pore structure within this range of temperature than the conventional porous glass composed mainly of silica.

The DTA curve shows transition points at 798°C and 856°C, the latter of which is the temperature at which 15 sintering begins to occur at the surface of glass. In view of the changes in TG it is believed that the OH's of Ti-OH and Si-OH will be lost at this temperature of 856°C.

As indicated above, it is to be appreciated that the porous titanate glass produced according to this invention 20 has a high heat resistance as well as a high chemical reactivity as the Ti-OH and Si-OH groups are retained until a higher temperature is reached.

Fig. 5 shows the chemical resistance (alkali resistance) of the porous titanate glass. To analyze the chemical 25 resistance, 1 g of porous titanate glass was placed on a

glass filter and immersed in a 1/4 normal NaOH solution kept at 40°C to measure the weight changes with time. The ordinate represents the weight of the porous titanate glass which remained on the filter while the abscissa represents
5 the immersion time.

The curve (a) represents a commercially available porous silica glass while the curve (b) represents a porous titanate glass according to this invention which was produced through a phase separation process at 720°C for 12 hours, followed
10 by annealing (strengthening) at 400°C for 12 hours. The curve (c) represents another porous titanate glass which was subjected to the same phase separation process but annealed (or subjected to strengthening treatment) at 700°C for 12 hours.

15 As is seen from the graph of Fig. 5, the commercially available porous silica glass (a) was completely dissolved after 100 hours of alkali leaching, whereas the porous titanate glass according to this invention provides a higher chemical resistance than the conventional porous silica glass in that
20 60% and 80% of the porous titanate glasses (b) and (c) which were subjected to annealing (strengthening treatment) at 400°C and 700°C, respectively remained undissolved after 100 hours of alkali leaching.

Example 2

25 Porous glasses were produced in the same manner as

described with respect to Example 1, using the starting materials (A) (Sample 2) and (B) (Sample 3) indicated in the left columns of Table 1 below. The compositions (weight %) of the resulting porous titanate glasses were shown in the right columns of Table 1.

Table 1

Components	Starting material composition (mol%)		Porous glass composition (wt%)	
	Sample 2 (A)	Sample 3 (B)	Sample 2 (A)	Sample 3 (B)
TiO ₂	17.0	26.0	46.3	58.8
SiO ₂	34.0	26.0	57.8	44.7
Al ₂ O ₃	13.0	10.0	0.1	0.4
B ₂ O ₃	7.0	5.0	0	0
CaO	24.0	28.0	0	0
MgO	5.0	5.0	0	0
Total	100.0	100.0	104.0	103.9

* Methods of analysis: gravimetric analysis for SiO₂; colorimetry for TiO₂; fluorometry for Al₂O₃; BF ion electrode method for B₂O₃; atomic-absorption spectroscopy for CaO, MgO.

As is seen from Table 1, the glass composition ratio (wt%) of titania to silica TiO₂/SiO₂ is 0.8 for Sample 2 and 1.3 for Sample 3.

In both Sample 2 and 3, as in Example 1, it was possible to control the pore size and specific surface area by adjusting the heat treatment conditions (heating temperature and time) as shown in Figs. 6 and 7. The heat treatment conditions and method of measurement were the same as with Example 1.

As is seen from Figs. 6 and 7, as the heat treatment temperature rises, the specific surface area decreases whereas the pore radius increases. It is thus possible to produce a porous titanate glass having any desired pore structure with a specific surface area ranging from $500 \text{ m}^2/\text{g}$ to $10 \text{ m}^2/\text{g}$ and a pore radius ranging from 20 \AA to 500 \AA (2 to 50 nm) by changing the heat treatment temperature (phase separation temperature) and heating time.

15 Example 3

One of the features of the present invention is to add a metallic element oxide such as MoO_3 , SeO_3 or Fe_2O_3 to the starting material composition and have such metallic element oxide supported on a glass skeleton. In conventional porous glass produced from oxide glass, most of any metallic element oxide incorporated in the starting materials is leached out by the acid treatment with only a trace amount thereof remaining. In contrast, according to the present invention, the metallic element oxide added to the starting material composition is not completely removed during the acid leaching

20
25

treatment but remains supported on the skeleton of porous titanate glass.

By way of example, MoO_3 was used as a metallic element oxide, and a porous titanate glass was produced from the starting material composition of 26.0 TiO_2 - 25.0 SiO_2 - 16.0 Al_2O_3 - 5.0 B_2O_3 - 24.5 CaO - 2.5 Na_2O - 1.0 MoO_3 (on a mol % basis). The chemical composition of the resulting porous titanate glass was as shown in Table 2 below, and the composition ratio (wt.%) of titania to silica was 1.7.

10

Table 2

Oxides	TiO_2	SiO_2	Al_2O_3	B_2O_3	CaO	Na_2O	MoO_3	Total
wt.%	63.8	38.6	0.2	0	0	0.1	1.2	103.9

It was confirmed from Table 2 that the added MoO_3 was contained in the porous titanate glass product. It is an important advantage in using the porous glass as a catalyst that such metallic element oxide can be supported on the porous carrier. It has also been found that the composition amounts of Al_2O_3 and Na_2O_3 would vary depending upon the phase separation and acid treatment conditions.

20

Example 4

As shown in Table 3 listed below, while according to the present invention, porous titanate glass may be produced fundamentally from a six-component system comprising TiO_2 - SiO_2 - Al_2O_3 - B_2O_3 - CaO - Na_2O (Samples 4-6), an equimolar

amount of Li_2O may be used in place of Na_2O (Sample 7). Alternatively, if 5.0 or more mol % of MgO is added, such porous titanate glass may be produced even from a composition of non-alkali metal oxides (Sample 8).

5 The added metallic element oxides (Samples 9-12 and 15) have the effect of reducing the cracking of the glass and enlarging the phase separation region of the glass. The amount of such metallic element oxides remaining in the porous titanate glass product vary depending on the heat treatment
10 conditions and metallic elements used.

 The amount of TiO_2 in the starting materials may be increased to such an extent that the molar ratio of SiO_2 to TiO_2 becomes about 0.4. However, if the ratio of $\text{SiO}_2/\text{TiO}_2$ is 1.0 or below, it is difficult to completely vitrify the
15 composition due to crystallization when the method of quenching the melt by depositing it in a water bath is utilized for the quenching step. With the $\text{SiO}_2/\text{TiO}_2$ ratio in the range from 1.0 to 2.0, the composition may be easily vitrified to obtain glass in the form of particles, sheet or hollow fiber.

Table 3

Sample	Starting material composition (mol %)								
	TiO ₂	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	MgO	Na ₂ O	Li ₂ O	Metallic Element Oxides
4	34.0	17.0	16.0	5.0	25.5	--	2.5	--	--
5	32.0	20.0	16.0	5.0	25.0	--	2.0	--	--
6	26.0	26.0	16.0	5.0	24.5	--	2.5	--	--
7	26.0	26.0	16.0	5.0	24.5	--	--	2.5	--
8	26.0	26.0	10.0	5.0	28.0	5.0	--	--	--
9	26.0	25.0	16.0	5.0	24.5	--	2.5	--	1.0 (MoO ₃)
10	26.0	25.0	16.0	5.0	24.5	--	--	2.5	1.0 (MoO ₃)
11	26.0	25.0	16.0	5.0	24.5	--	2.5	--	1.0 (SeO ₃)
12	26.0	25.0	16.0	5.0	24.5	--	2.5	--	1.0 (Fe ₂ O ₃)
13	17.0	34.0	16.0	5.0	25.0	--	2.5	--	--
14	17.0	34.0	13.0	7.0	24.0	5.0	--	--	--
15	17.0	34.0	12.0	7.0	24.0	5.0	--	--	1.0 (MoO ₃)
16	17.0	34.0	13.0	5.0	24.5	5.0	2.5	--	--
Control									
1	10.0	42.0	16.0	5.0	24.5	--	2.5	--	--
2	7.5	44.5	16.0	5.0	24.5	--	2.5	--	--
3	5.0	47.0	16.0	5.0	24.5	--	2.5	--	--

With the starting material compositions shown as Controls 1 and 2, an opaline separate-phase glass was obtained by the heat treatment, but it was completely dissolved by the acid treatment so that no porous glass was produced. With the 5 starting material composition shown as Control 3, it did not produce any opaline separate-phase glass so that no porous glass could be obtained.

The pore distribution, heat resistance and chemical resistance of porous titanate glasses produced from the 10 starting material compositions shown in the aforesaid examples will be discussed below.

Fig. 8 shows the pore distributions of the porous titanate glass of the Sample 8 (same as the Sample 3 shown in Table 1) as measured using a soaped mat manufactured by 15 Carlo Elba Corp., Italy. The solid line curve (a), broken line curve (b) and chain line curve (c) show the pore distributions for the glasses produced under different heat treatment conditions for the phase separation. Specifically, the heat treatment conditions were 700°C and 15 hours for 20 the glass (a); 720°C and 15 hours for the glass (b); and 740°C and 15 hours for the glass (c). With the heat treatment (a) at 700°C for 15 hours, there are a considerable number of pores having a radius on the order of 20 Å, (2 nm), whereas with the heat treatment (c) at 740°C for 15 hours, there 25 are pores of radius 80 Å (8 nm) and 150 to 250 Å (15 to 25 nm), but no pores having a radius

on the order of 20 \AA (2 nm). It is to be understood that the pore size increases with a rise in the heat treatment temperature.

Upon analyzing the weight changes versus temperature changes, namely the heat resistance of the porous titanate glass produced from the starting material composition shown in the Sample 7, the same results as those shown in Fig. 4 were obtained. It was thus seen that the porous titanate glass produced according to this invention had a higher heat resistance and a more stable pore structure than the conventional porous glass composed mainly of silica as well as having a high chemical reactivity as the Ti-OH and Si-OH groups were retained until a higher temperature was reached.

Fig. 9 shows the chemical resistance (alkali resistance) of the porous titanate glass. These results were obtained by placing 1 g of porous titanate glass on a glass filter and immersing it in a 1/4 normal NaOH solution kept at 40°C to measure the weight changes with time. The ordinate of the graph represents the weight of the porous titanate glass which remained on the filter while the abscissa represents the immersion time.

The curve (a) represents a commercially available porous silica glass while the curve (b) represents a porous titanate glass which was produced by subjecting the fused glass of the Sample 6 to phase separation treatment at 720°C for 12 hours. The glass was annealed or subjected to strengthening process

at 400°C for 12 hours. The curve (c) represents the porous titanate glass which is the same as that of (b) but which was annealed or subjected to strengthening treatment at 700°C for 12 hours. The curve (d) represents a porous titanate
5 glass which was produced from the starting material composition shown in Sample 7 and which was annealed or subjected to strengthening treatment at 700°C for 12 hours.

As is seen from the graph of Fig. 9, the commercially available porous silica glass (a) was completely dissolved
10 after 100 hours of alkali leaching, whereas the porous titanate glass according to this invention provides a higher chemical resistance than the conventional porous silica glass in that 60% to 80% of the porous titanate glasses (b), (c) and (d) which were subjected to annealing or strengthening treatment
15 at 400°C and 700°C, respectively remained undissolved after 100 hours of alkali leaching.

The preferred material compositions for producing a sheet and fibers of porous titanate glass according to the present invention, and such material compositions having metallic
20 element oxide added thereto are shown in Tables 4 and 5, respectively.

With the materials in the range of composition as shown, the fusing step is facilitated, crystallization is very unlikely to occur during the quench-vitrification step, cracking
25 and delaminating are minimized during the acid treating step,

and it is possible to manufacture a homogeneous quality of porous titanate glass in sheet form in a short time.

Table 4

Material	TiO ₂	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	MgO
1	18.0	38.0	10.0	7.5	21.0	4.5
2	21.0	35.0	12.5	7.5	21.5	2.5
3	23.0	33.0	12.5	7.5	21.5	2.5
4	25.0	31.0	12.5	7.5	22.5	1.5
5	28.0	28.0	12.5	7.5	22.5	1.5

Table 5

Materials	TiO ₂	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	MgO	Metallic element oxides
6	25.0	30.5	12.5	7.5	22.5	1.5	0.5 (MoO ₃)
7	25.0	30.5	12.5	7.5	22.5	1.5	0.5 (SeO ₂)
8	25.0	30.5	12.5	7.5	22.5	1.5	0.5 (Ni ₂ O ₃)
9	25.5	30.5	12.5	7.5	21.5	1.5	1.0 (Ni ₂ O ₃)
10	25.5	30.5	12.5	7.5	21.5	1.5	1.0 (MoO ₃)

Example 5

This example is illustrative of the method of producing a sheet of porous titanate glass according to the present invention.

5 Starting materials used were of the composition (4 in Table 4) which comprised 25.0 TiO_2 , 31.0 SiO_2 , 12.5 Al_2O_3 , 7.5 B_2O_3 , 22.5 CaO , and 1.5 MgO (mol composition). These materials were thoroughly mixed together in a ball mill or the like. The mixture was then fused by heating in an electric
10 furnace at 1,400°C for 30 to 60 minutes, quenched by placing it in a water bath, and shaped (rolled) to form a transparent sheet of glass. Then, as the sheet of glass was heated at a temperature of 600°C to 900°C, preferably 700°C to 850°C, more preferably 750°C to 800°C for a predetermined period of
15 time in the range of 4 to 12 hours, the glass was changed from its transparent state to an opaline or devitrified state whereby a separate-phase glass in sheet form was obtained. This separate-phase glass was immersed in a hydrochloric acid solution of 0.5N - 1.0N at 90°C for 1 to 12 hours to leach
20 out and remove acid-soluble components, whereby a sheet of porous glass with a glass skeleton of acid-insoluble TiO_2 and SiO_2 remaining was produced. The porous glass was dried in a vacuum at 110°C, and was then annealed or subjected to strengthening treatment at 700°C as required.

25 It was found that the thus produced porous titanate glass

had a composition (weight %) of 37.5 TiO_2 - 46.0 SiO_2 - 14.3 Al_2O_3 - 2.17 CaO .

The composition analysis of the foregoing starting materials and porous titanate glass was carried out by X-ray fluorescence analysis .

Example 6

This example is illustrative of the method of producing porous titanate glass in fibrous form according to the present invention.

10 Starting materials used were of the composition (4 in Table 4) which comprised 25.0 TiO_2 , 31.0 SiO_2 , 12.5 Al_2O_3 , 7.5 B_2O_3 , 22.5 CaO , and 1.5 MgO (mol composition). These materials were thoroughly mixed together in a ball mill or the like. The mixture was fused by heating in an electric
15 furnace at 1,400°C for 30 to 60 minutes.

The thus fused mixture was spun by a conventional solution spinning process and quenched to form transparent glass in fibrous form.

Then, as the transparent glass in fibrous form was heated
20 at a temperature of 600°C to 900°C, preferably 700°C to 850°C, more preferably 750°C to 800°C for a predetermined period of time in the range of 4 to 12 hours, the glass was changed from its transparent state to an opaline or devitrified state whereby a separate-phase glass in fibrous form was obtained. This
25 separate-phase glass was immersed in a hydrochloric acid

solution of 0.5 N - 1.0 N at 90°C for 1 to 12 hours to leach out and remove solid-soluble components, whereby porous glass fibers with a glass skeleton of acid-insoluble TiO_2 and SiO_2 remaining was produced. Subsequently, the porous
 5 glass fibers were immersed in a titanium tetrahydroxide (Ti(OH)_4) solution and then dried in a vacuum at 110°C, followed by annealing or strengthening treatment at 700°C as required. This immersion treatment in titanium tetrahydroxide (Ti(OH)_4) solution may be omitted. Titanium
 10 tetrachloride (TiCl_4) or Titanium alcoxide (Ti(O-R)_4 wherein R is alkyl group) may be used in substitution for titanium tetrahydride (Ti(OH)_4).

It was found that the thus produced porous titanate glass fibers had a composition (weight %) of 37.5 TiO_2 - 46.0 SiO_2
 15 - 14.3 Al_2O_3 - 2.17 CaO.

The composition analysis of the foregoing starting materials and porous titanate glass was carried out by X-ray fluorescence analysis.

It is to be understood that the spinning process in
 20 producing porous titanate glass in fibrous form is not limited to the solution spinning method as described above but may be carried out any suitable method.

While the diameter of glass fibers produced may vary depending upon the spinning method employed, short fibers on
 25 the order of 0.5 mm in length may generally have a diameter

of less than several 5 μm , and long fibers may have a diameter greater than 15 \AA (1.5 nm).

The foregoing porous glass has a glass skeleton composed of titania and silica and exhibits high heat resistance and chemical
5 resistance (alkali resistance) as well as high chemical reactivity. The porous titanate glass is suitable for use inter alia as an adsorbent, catalyst, catalyst support, gas sensor, ultrafiltration medium, reaction separating membrane, and carrier for immobilized enzymes.

Claims:

1. Porous titanate glass characterized by having a glass skeleton composed mainly of titania (TiO_2) and silica (SiO_2).
- 5 2. The glass according to claim 1, wherein the glass composition ratio (weight %) $\text{TiO}_2/\text{SiO}_2$ is in the range of 0.8 to 1.7.
3. The glass according to claim 1 or claim 2, which is in the form of a sheet or is in the form
10 of fibers.
4. A method of producing a porous titanate glass having a glass skeleton composed mainly of titania and silica, the method comprising the steps of:
mixing starting materials containing titanium oxide,
15 silicic anhydride, aluminum oxide, boron oxide, and calcium oxide; heating and fusing the mixture, then quenching it to form a multi-component oxide glass composed of vitrified $\text{TiO}_2 - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{CaO}$; reheating the said oxide glass at a temperature of
20 600°C to 900°C for a predetermined period of time to form an opaline or devitrified separate-phase glass; and immersing the separate-phase glass in an acid solution to leach out and remove acid-soluble components.
- 25 5. The method of claim 4, wherein said

starting materials contain about 25.0 mol % of titanium oxide, 31.0 mol % of silicic anhydride, 12.5 mol % of aluminium oxide, 7.5 mol % of boron oxide, and 24.0 mol % of calcium oxide.

- 5 6. A method according to claim 4, wherein the starting materials contain titanium oxide, silicic anhydride, aluminum oxide, boron oxide and calcium oxide as principal components and at least one accessory component selected from magnesium oxide, 10 alkali metal oxide and metallic element oxide so as to form, after heating, fusing and quenching a multi-component oxide glass composed of vitrified
- $$\text{TiO}_2 - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{CaO} - \text{MgO} \text{ and/or}$$
- $$\text{X}_2\text{O} \text{ and/or } \text{Y}_m\text{O}_n \text{ (wherein } \text{X}_2\text{O} \text{ is alkali metal oxide}$$
- 15 and Y_mO_n is metallic element oxide).

7. The method according to claim 6, wherein the starting materials contain 15 to 34 mol % of titanium oxide, 17 to 34 mol % of silicic anhydride, 5 to 20 mol % of aluminum oxide, 1 to 10 mol % of 20 boron oxide, 10 to 30 mol % of calcium oxide, 10 or less mol % of magnesium oxide, 5 or less mol % of alkali metal oxide, and 5 or less mol % of metallic element oxide, the ratio of silicic anhydride to titanic oxide ($\text{SiO}_2/\text{TiO}_2$) for example being 0.4 to 2.0.

- 25 8. A method of producing porous titanate glass

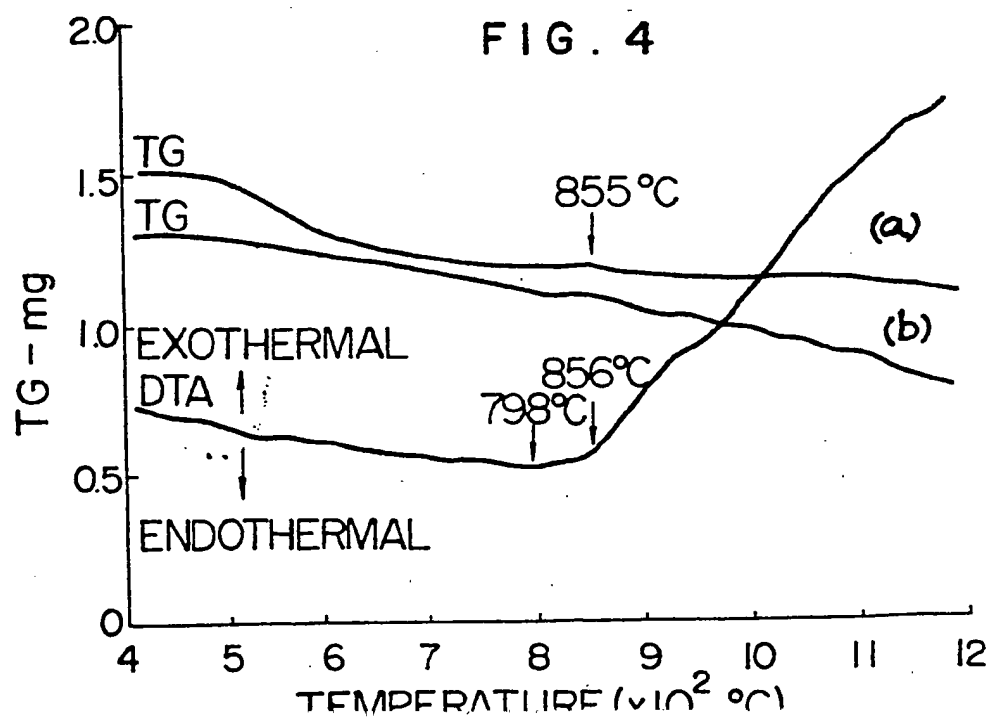
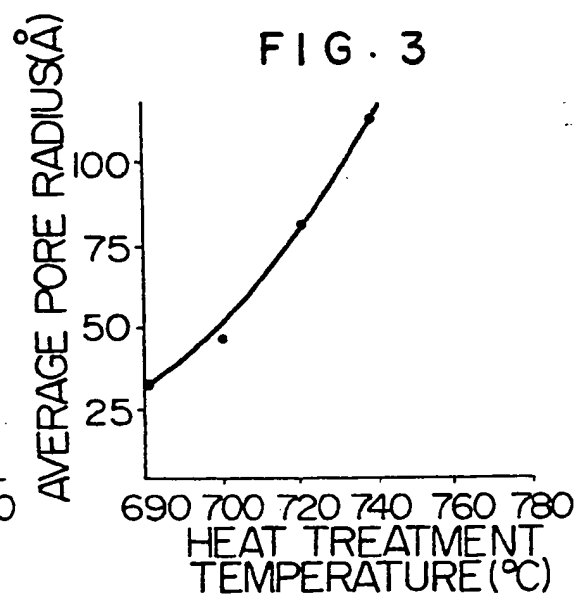
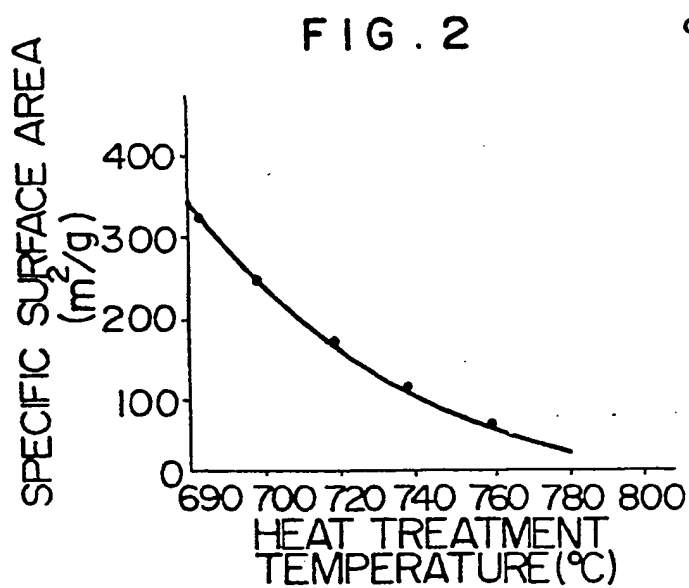
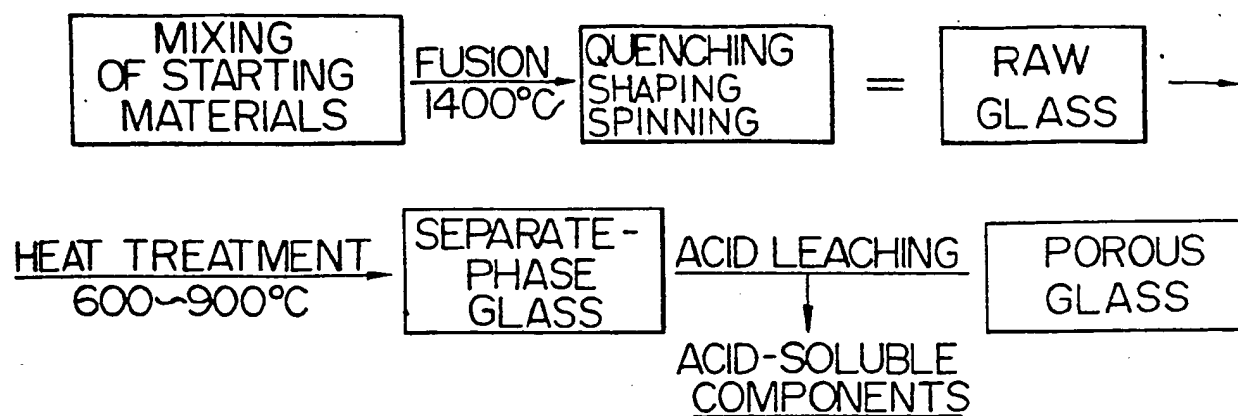
having a glass skeleton composed mainly of titania and silica, in sheet or fiber form, said method comprising the steps of: mixing starting materials containing titanium oxide, silicic anhydride, aluminum oxide, boron oxide, calcium oxide and magnesium oxide, and if desired, metallic element oxide so that the composition of the mixture on the basis of mol % of the oxides is such that $(\text{TiO}_2 + \text{SiO}_2)/(\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3 + \text{CaO} + \text{MgO})$ is 1.20 - 1.40, $\text{TiO}_2/\text{SiO}_2$ is 0.5 - 1.0, $\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3$ is 1.0 - 0.6 and MgO/CaO is 0.21 - 0.06; heating and fusing the mixture; then quenching and shaping it to form a sheet of multi-component oxide glass, or spinning and quenching it to form fibers of said glass, which is composed of vitrified $\text{TiO}_2 - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{CaO} - \text{MgO} - \text{Y}_m\text{O}_n$ (metallic element oxide when used); reheating said oxide glass in sheet or fiber form at a temperature of 600°C to 900°C for a predetermined period of time to form an opaline or divitrified separate-phase glass; and then immersing said separate-phase glass in an acid solution to leach out and remove acid-soluble components.

9. The method according to claim 8, wherein said starting materials contain 18.0 - 28.0 mol % of titanium oxide, 38.0 - 28.0 mol % of silicic anhydride, 10.0 - 12.5 mol % of aluminum oxide, 7.5 mol % of boron oxide, 21.0 - 22.5 mol % of calcium oxide and

4.5 - 1.5 mol % of magnesium oxide.

10. The method according to claim 8 or claim 9, wherein said metallic element oxide, when used, is 0.5 - 1.0 mol % of MoO_3 , SeO_3 or Ni_2O_3 .

FIG. 1



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FIG. 5

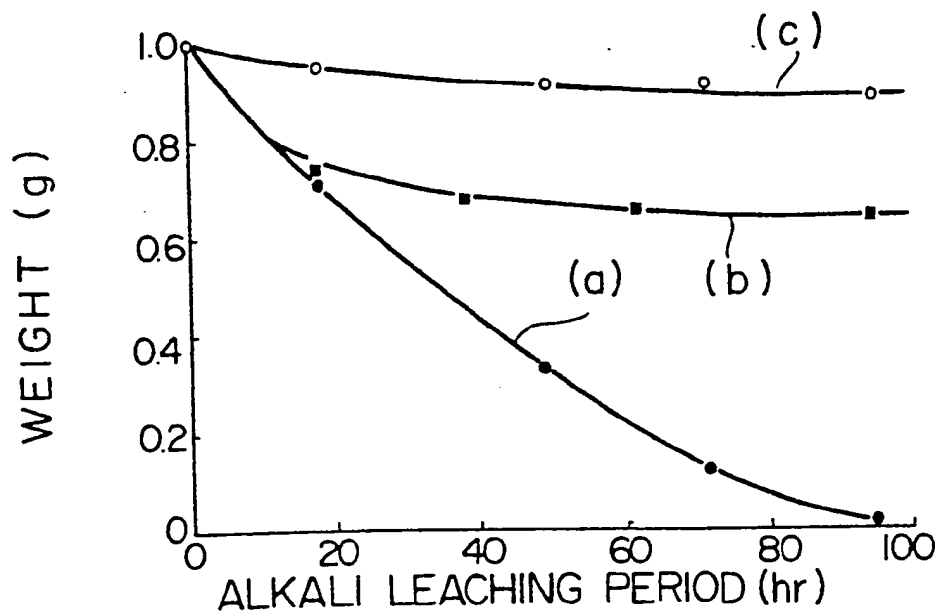


FIG. 6

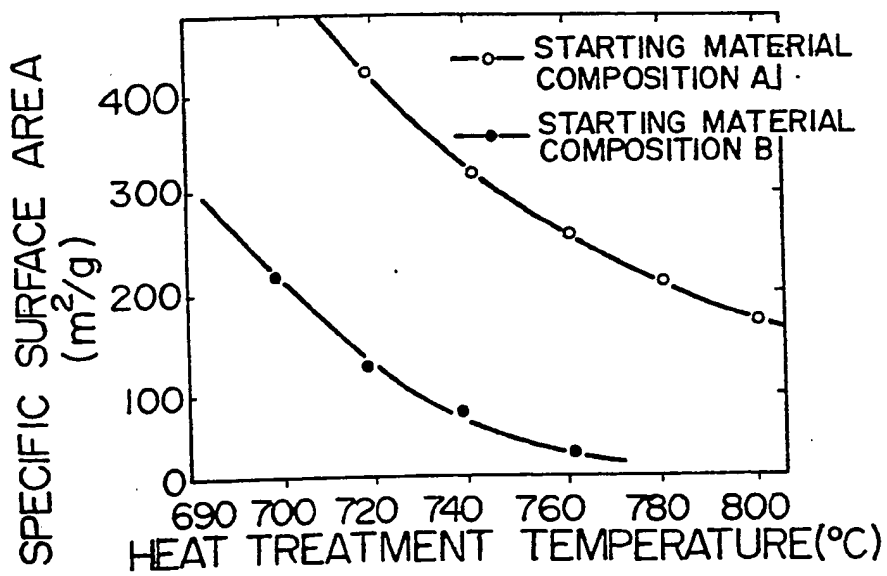


FIG. 7

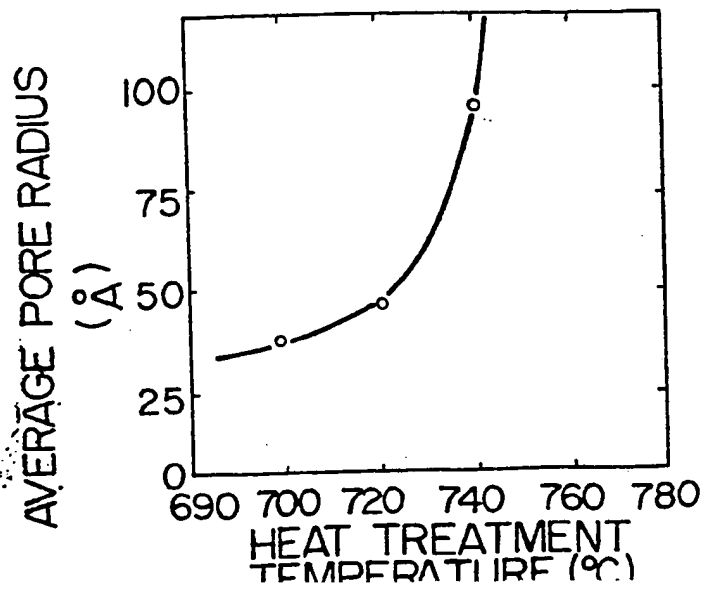


FIG. 8

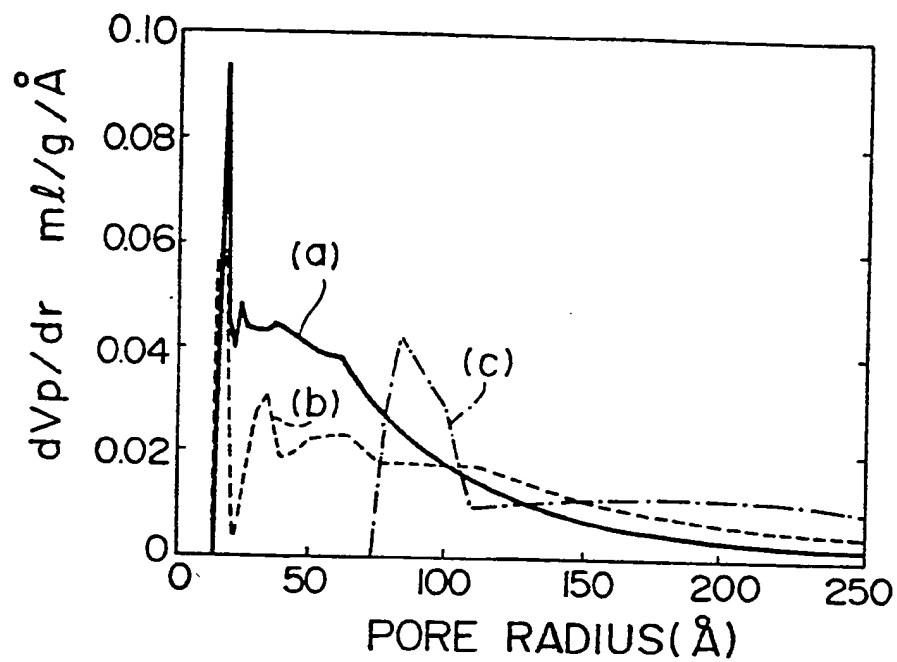
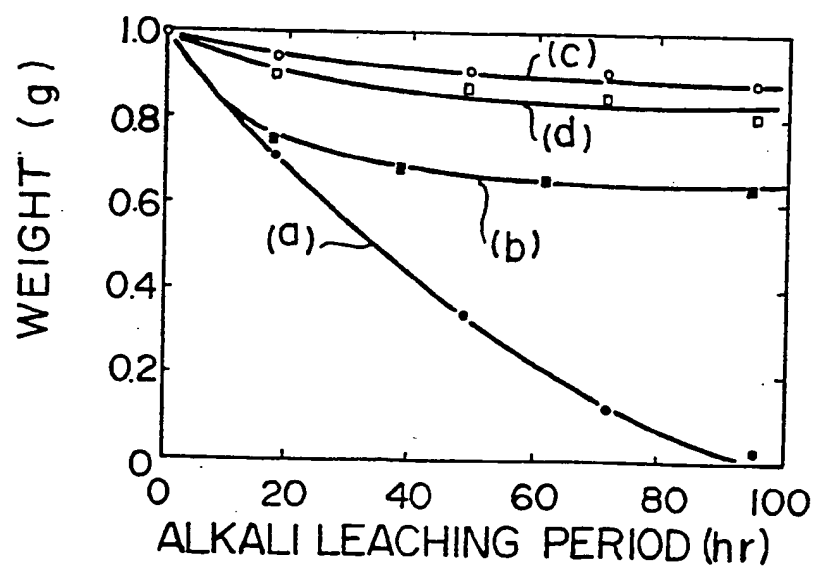


FIG. 9





European Patent
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EUROPEAN SEARCH REPORT

0174851
Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 85306475.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	AT - B - 299 435 (FARBENFABRIKEN BAYER) * Claims 1,2; page 6, example 9; page 4, line 51 - page 5, line 6 * --	1-3	C 03 C 3/04 C 03 C 3/064 C 03 C 3/091 C 03 C 13/02 C 03 C 10/00 C 03 C 11/00 C 03 C 15/00 C 03 C 25/06
Y	GB - A - 1 077 195 (GLAVERBEL) * Claims 1-7; page 4, example 2 * --	4-9	/B 01 J 20/10 B 01 J 21/06 B 01 J 32/00 B 01 D 13/04 C 12 N 11/14
Y	US - A - 3 650 721 (HAMMEL) * Claims * -----	4-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 03 C C 03 B D 01 F B 01 J B 01 D C 12 N
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 29-11-1985	Examiner HAUSWIRTH
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technical background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			